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FILE 'HOME' ENTERED AT 18:38:12 ON 29 SEP 2005
=> Index chemistry bioscience dissabs
FILE 'ENCOMPLIT2' ACCESS NOT AUTHORIZED
FILE 'DRUGMONOG' ACCESS NOT AUTHORIZED
COST IN U.S. DOLLARS
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                                                                SESSION
FULL ESTIMATED COST
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INDEX 'AGRICOLA, ALUMINIUM, ANABSTR, APOLLIT, AQUALINE, AQUIRE, BABS,
       BIOCOMMERCE, BIOTECHNO, CABA, CAOLD, CAPLUS, CBNB, CEABA-VTB, CEN, CERAB,
       CIN, COMPENDEX, CONFSCI, COPPERLIT, CORROSION, DISSABS, ENCOMPLIT,
       FEDRIP, GENBANK, INSPEC, INSPHYS, INVESTEXT, ...'
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98 FILES IN THE FILE LIST IN STNINDEX
Enter SET DETAIL ON to see search term postings or to view
search error messages that display as 0* with SET DETAIL OFF.
=> s (rhodium or ruthenium or palladium) (P) ((complex? or coordinat? or bind? or bound) (s)
(myoglobin or hemoglobin or hemeoxygenase catalase or cytochrome or ferritin ))
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FILE WSCA

FILE ANTE FILE AQUASCI

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           FILE EMBASE
      57* FILE ESBIOBASE
       0* FILE FOMAD
       0* FILE FOREGE
       0* FILE FROSTI
       0* FILE FSTA
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         FILE IFIPAT
      14
75 FILES SEARCHED...
      32 FILE LIFESCI
         FILE MEDLINE
      64
       0* FILE NUTRACEUT
       0* FILE PHARMAML
          FILE TOXCENTER
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      59
         FILE USPATFULL
       1
          FILE USPAT2
94 FILES SEARCHED...
      19 FILE WPIDS
           FILE WPINDEX
      19
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- 41 FILES HAVE ONE OR MORE ANSWERS, 98 FILES SEARCHED IN STNINDEX
- L1 QUE (RHODIUM OR RUTHENIUM OR PALLADIUM) (P) ((COMPLEX? OR COORDINAT? OR BI ND? OR BOUND) (S) (MYOGLOBIN OR HEMOGLOBIN OR HEMEOXYGENASE CATALASE O R CYTOCHROME OR FERRITIN ))

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F2
           96
               SCISEARCH
F3
           86
                BIOSIS
F4
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                MEDLINE
F5
           63
                EMBASE
F6
           59
                USPATFULL
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F7
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           57* ESBIOBASE
F8
           42* PASCAL
F9
           34* BIOTECHNO
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                JICST-EPLUS
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213

CAPLUS

=> d rank F1

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F40
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F41
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FILE 'CAPLUS' ENTERED AT 18:47:35 ON 29 SEP 2005
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FILE 'CABA' ENTERED AT 18:47:35 ON 29 SEP 2005
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FILE 'CANCERLIT' ENTERED AT 18:47:35 ON 29 SEP 2005
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L2
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             O FILE SCISEARCH
L4
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             O FILE MEDLINE
             0 FILE EMBASE
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L5 L6 L7 2 FILE DISSABS L8 O FILE JICST-EPLUS L9 0 FILE LIFESCI L10 O FILE TOXCENTER Lll O FILE WPIDS L12 O FILE IFIPAT L13 0 FILE CABA L14 0 FILE CANCERLIT

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11 L1 AND PHOSPHIN?
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            41 FILE SCISEARCH
L17
L18
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            29 FILE MEDLINE
L19
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L27
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            0 FILE JICST-EPLUS
            O FILE LIFESCI
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T<sub>2</sub>40
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T.42
             0 FILE CANCERLIT
TOTAL FOR ALL FILES
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L43
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PROCESSING COMPLETED FOR L29
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=> D L15 1-11 ibib abs
L15 ANSWER 1 OF 11 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER:
                         2005:185451 CAPLUS
DOCUMENT NUMBER:
                         142:276006
TITLE:
                         Preparation of a metal complex-protein composite for
                         the use as a hydrogenation catalyst of an olefin
                         Watanabe, Yoshihito; Ueno, Takafumi; Abe, Satoshi
INVENTOR(S):
PATENT ASSIGNEE(S):
                         Nagoya Industrial Science Research Institute, Japan
SOURCE:
                         U.S. Pat. Appl. Publ., 7 pp.
                         CODEN: USXXCO
DOCUMENT TYPE:
                         Patent
LANGUAGE:
                         English
FAMILY ACC. NUM. COUNT:
PATENT INFORMATION:
     PATENT NO.
                         KIND
                                            APPLICATION NO.
                                DATE
                                                                   DATE
                         _ _ _ _
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                                                                   _____
     US 2005049405
                                            US 2004-790060
                          A1
                                20050303
                                                                   20040302
     JP 2005075799
                         A2
                                20050324
                                            JP 2003-310085
                                                                   20030902
PRIORITY APPLN. INFO.:
                                            JP 2003-310085
                                                                A 20030902
OTHER SOURCE(S):
                        MARPAT 142:276006
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TOTAL FOR ALL FILES

AB The metal complex-protein composite of the present invention includes a protein having a cavity and a metal complex and has a specific structure that the metal complex is received in the cavity of the protein. Here the metal complex is prepared by complexation of a metal ion, which is selected

among the group consisting of rhodium, ruthenium, and palladium, with a ligand. The metal complex-protein composite of the invention functions as a hydrogenation catalyst of an olefin in water. The metal complex-protein composite is thus effectively applied to hydrogenation of water-soluble substrates and has environmental advantages over organic solvents. Preparation of rhodium complexes-apomyoglobin composites and their use as hydrogenation catalysts of olefins is disclosed.

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L15 ANSWER 2 OF 11 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER:
                         2004:734455 CAPLUS
DOCUMENT NUMBER:
                         142:168270
TITLE:
                         Palladium(II) and platinum(II) complexes with mixed
                         ligands of tertiary monophosphines and
                          5-phenyl-1,3,4-oxadiazole-2-thione or
                          4,5-diphenyl-1,2,4-triazole-3-thione
                         Qadir, Adnan M.; Abdullah, Ali I.; Al-jibor, Subhi A.;
AUTHOR(S):
                         Al-Allaf, Talal A. K.
                         Department of Chemistry, College of Basic Sciences,
CORPORATE SOURCE:
                         Applied Science University, Amman, 1193, Jordan
                         Asian Journal of Chemistry (2004), 16(2), 1181-1188
SOURCE:
                         CODEN: AJCHEW; ISSN: 0970-7077
PUBLISHER:
                         Asian Journal of Chemistry
DOCUMENT TYPE:
                         Journal
LANGUAGE:
                         English
     Several new palladium(II) and platinum(II) complexes
     containing two types of ligands: tertiary monophosphines (L) and
     5-phenyl-1,3,4-oxadiazole-2-thione (HA) or 4,5-diphenyl-1,2,4-triazole-3-
     thione (HB) were prepared The so obtained complexes
     trans-[PdA2L2], trans-[PdB2L2] and cis-[PtA2L2] were characterized by
     elemental anal., IR, UV-visible, 31P NMR spectroscopy, molar conductance
     and magnetic susceptibility measurements.
                                THERE ARE 20 CITED REFERENCES AVAILABLE FOR THIS
REFERENCE COUNT:
                         20
                                RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT
L15 ANSWER 3 OF 11 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER:
                          2004:156420 CAPLUS
DOCUMENT NUMBER:
                          141:174283
                         A series of vinylidene-, vinyl-, carbene- and
TITLE:
                          carbyneruthenium(II) complexes with [Ru(PCy3)2] and
                          [Ru(PiPr3)2] as molecular building blocks
AUTHOR (S):
                          Jung, Stefan; Ilg, Kerstin; Brandt, Carsten D.; Wolf,
                          Justin; Werner, Helmut
                          Institut fuer Anorganische Chemie der Universitaet
CORPORATE SOURCE:
                          Wuerzburg, Wuerzburg, 97074, Germany
SOURCE:
                          European Journal of Inorganic Chemistry (2004), (3),
                          469-480
                          CODEN: EJICFO; ISSN: 1434-1948
PUBLISHER:
                          Wiley-VCH Verlag GmbH & Co. KGaA
DOCUMENT TYPE:
                          Journal
LANGUAGE:
                          English
                          CASREACT 141:174283
OTHER SOURCE(S):
     The hydrido(vinylidene) complexes [RuHCl(:C:CHR)(L)2] (R = H, tBu, Ph; L =
     PCy3, PiPr3) undergo metathesis reactions in the presence of KX (X = I, I)
     NCO, OPh, CH3CO2, CF3CO2) to give the substitution products
     [RuHX(:C:CHR)(L)2] in good to excellent yields. Treatment of
     [RuHX(:C:CHR)(L)2] with HBF4 in di-Et ether affords the cationic
     carbyneruthenium(II) derivs. [RuHX(.tplbond.CCH2R)(OEt2)(L)2]BF4 and
     [RuH(\kappa2-O2CCH3)(.tplbond.CCH2R)(L)2]BF4. The reactions of [RuHCl(:C:CHR)(L)2] with MX [X = BF4, PF6, BPh4, B(Arf)4] in acetonitrile
     lead to the formation of cationic five- and six-coordinate
     vinylruthenium(II) compds. of which [Ru(CH:CH2)(CH3CN)2(PCy3)2]BPh4 has
     been characterized by x-ray crystallog. The starting material
     [RuHCl(:C:CHPh)(PiPr3)2] reacts with CO to give
     [RuCl(CH:CHPh)(CO)2(PiPr3)2] and with N2 to produce
     [RuCl(CH:CHPh)(N2)(PiPr3)2] (crystal structure). Protonation of
     [Ru(CH:CH2)(CH3CN)2(PCy3)2]X and [Ru(CH:CHPh)(CH3CN)3(PiPr3)2]X with HBF4
     and HB(Arf)4 yields the dicationic carbene ruthenium
     (II) complexes [Ru(:CHCH3)(CH3CN)2(PCy3)2]X2 and
```

[Ru(:CHCH2Ph)(CH3CN)3(PiPr3)2] [B(Arf)4]2, the latter of which eliminates

styrene to give [Ru(CH3CN)3(PiPr3)2][B(Arf)4]2.

REFERENCE COUNT: 40 THERE ARE 40 CITED REFERENCES AVAILABLE FOR THIS

RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 4 OF 11 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 2002:682077 CAPLUS

DOCUMENT NUMBER: 138:347831

TITLE: Compounds of general interest.

Chloro(hydrotris(pyrazol-1-

yl)borato)bis(triphenylphosphine)ruthenium(II) {RuCl[k3-HB(pz)3](PPh3)2} (pz = pyrazol-1-yl) Hill, Anthony F.; Wilton-Ely, James D. E. T.;

Rauchfuss, Thomas B.; Schwartz, Daniel E.

CORPORATE SOURCE: Department of Chemistry, Imperial College of Science,

Technology and Medicine, London, SW7 2AY, UK

SOURCE: Inorganic Syntheses (2002), 33, 206-208

CODEN: INSYA3; ISSN: 0073-8077

PUBLISHER: John Wiley & Sons, Inc.

DOCUMENT TYPE: Journal LANGUAGE: English

AUTHOR(S):

SOURCE:

OTHER SOURCE(S): CASREACT 138:347831

AB RuCl  $[\kappa 3 - HB(pz) 3]$  (PPh3) 2 complex was synthesized

on a large scale (10 g) and was characterized. The procedure is based on

the reaction of dichlorotris(triphenylphosphine)ruthenium(II)

with hydrotris(pyrazol-1-yl)borate K salt.

REFERENCE COUNT: 6 THERE ARE 6 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 5 OF 11 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1999:639825 CAPLUS

DOCUMENT NUMBER: 131:345704

TITLE: The sting of the scorpion: a metallaboratrane

AUTHOR(S): Hill, Anthony F.; Owen, Gareth R.; White, Andrew J.

P.; Williams, David J.

CORPORATE SOURCE: Department of Chemistry, Imperial College of Science,

Technology, and Medicine, London, SW72AY, UK
Angewandte Chemie, International Edition (1999),

38(18), 2759-2761

CODEN: ACIEF5; ISSN: 1433-7851

PUBLISHER: Wiley-VCH Verlag GmbH

DOCUMENT TYPE: Journal LANGUAGE: English

AB The novel ruthenaboratrane **complex**  $[Ru\{B(mt)3\}(CO)(PPh3)]$  (4, mt = 2-sulfanyl-1-methylimidazolyl) was prepared from the reaction of

[Ru(CH:CHCPh2OH)Cl(CO)(PPh3)2] with Na[HB(mt)3] and

characterized spectroscopically and by x-ray crystallog. (4·2CHCl3: triclinic, space group P.hivin.1, R1 = 0.049). The complex has a

Ru $\rightarrow$ B bond of 2.161(5) Å, resulting in a tetrahedral geometry for boron, and **ruthenium** is octahedral. This complex is the

first example of a poly(azolyl)borate ligand that undergoes B-H activation (stinging of the "scorpionate") to give this metallaboratrane structure.

REFERENCE COUNT:

SOURCE:

15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 6 OF 11 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1998:184831 CAPLUS

DOCUMENT NUMBER: 128:270700

TITLE: Polyazolyl Chelate Chemistry. 6. Bidentate

Coordination of HB(pz)3 (pz =

Pyrazol-1-yl) to **Ruthenium** and Osmium: Crystal Structure of [RuH(CO)(PPh3)2{κ2-

HB(pz)3

AUTHOR(S): Burns, Ian D.; Hill, Anthony F.; White, Andrew J. P.;

Williams, David J.; Wilton-Ely, James D. E. T.

CORPORATE SOURCE: Department of Chemistry, Imperial College of Science

Technology and Medicine, London, SW7 2AY, UK

Organometallics (1998), 17(8), 1552-1557

CODEN: ORGND7; ISSN: 0276-7333

PUBLISHER: American Chemical Society

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DOCUMENT TYPE:
                         Journal
LANGUAGE:
                         English
     The reactions of [RuHCl(CO)(PPh3)3], [Ru(SnPh3)Cl(CO)(PPh3)2], or
     [RuH(CO)(NCMe) 2(PPh3) 2]BF4 with K[HB(pz) 3] (pz = pyrazol-1-yl) provide the
     crystallog. characterized complex [RuH(CO)(PPh3)2{η2-HB(pz)3}],
     thermolysis of which proceeds via loss of phosphine and
     formation of [RuH(CO)(PPh3){\eta3-HB(pz)3}]. The thiocarbonyl analog
     [RuH(CS)(PPh3)2\{\eta 2\text{-HB}(pz)3\}] is similarly obtained by the reaction of
     [RuHCl(CS)(PPh3)3] and K[HB(pz)3], thermolysis of which provides
     [RuH(CS)(PPh3) \{ \eta 3 - HB(pz) 3 \}]. Hydride metathesis in CHCl3 of this
     species provides [RuCl(CS)(PPh3) \{\eta 3-HB(pz)3\}]. [RuH(CS)(PPh3)2 \{\eta 2-HB(pz)3\}]
     H2B(bta)2}] (bta = benzotriazolyl) results from the reaction of
     [RuHCl(CS)(PPh3)3] with K[H2B(bta)2]. The hydride-bridged dinuclear
     complex [RuCu(\mu-H)(CO)(PPh3)2{\eta3-HB(pz)3}]PF6 results in high yield
     from the reaction of [RuH(CO)(PPh3)2{\eta2-HB(pz)3}], with
     [Cu(NCMe)4]BF4. The \sigma-Ph complex [OsPh(CO)(PPh3)2\{\eta 2-HB(pz)3\}]
     results from the reaction of [OsPhCl(CO)(PPh3)2] with K[HB(pz)3] and is
     cleanly converted with heating to [OsPh(CO)(PPh3) {η3-HB(pz)3}].
REFERENCE COUNT:
                         59
                                THERE ARE 59 CITED REFERENCES AVAILABLE FOR THIS
                                RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT
L15 ANSWER 7 OF 11 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER:
                         1997:441104 CAPLUS
DOCUMENT NUMBER:
                          127:144294
                          Synthesis and reactivity of
TITLE:
                          [Ru\{HB(pz)3\}\{P(C6H11)3\}Cl(OCH2R)] (pz = pyrazolyl, R =
AUTHOR (S):
                          Gemel, Christian; Kickelbick, Guido; Schmid, Roland;
                          Kirchner, Karl
CORPORATE SOURCE:
                          Institute of Inorganic Chemistry, Technical University
                          of Vienna, Vienna, A-1060, Austria
                          Journal of the Chemical Society, Dalton Transactions:
SOURCE:
                          Inorganic Chemistry (1997), (12), 2113-2117
                          CODEN: JCDTBI; ISSN: 0300-9246
PUBLISHER:
                          Royal Society of Chemistry
DOCUMENT TYPE:
                          Journal
LANGUAGE:
                          English
     [Ru{HB(pz)3}(cod)Cl] (1) (cod = cycloocta-1,5-diene) reacted
     with P(C6H11)3 (≥1 equiv) in boiling DMF to give the highly
     air-sensitive intermediate [Ru{HB(pz)3}{P(C6H11)3}Cl(DMF)]
     which, on exposure to air in either ethanol or methanol as the solvent,
     was converted to the ruthenium(III) complexes [Ru{
     HB(pz)3{P(C6H11)3}C1(OCH2R)] (R = Me 2a or H 2b) in good yields.
     2B was characterized by x-ray crystallog. (triclinic, space group
     P.hivin.1, R = 0.038). Treatment of 2a or 2b with L = MeCN, pyridine, CO,
     P(OMe)3, or PMe3 in CH2Cl2 afforded the (diamagnetic) ruthenium
     (II) compds. [Ru\{HB(pz)3\}\{P(C6H11)3\}(C1)L] (3-7). Most remarkably, 2a or
     2b reacted also with terminal alkynes HC.tplbond.CR (R = Ph, CO2Et, Bu or
     SiMe3) giving the neutral vinylidene complexes [Ru{HB
     (pz)3{P(C6H11)3}Cl(=C=CHR)] (8-11). Preliminary results of a study of
     the catalytic activity of 2 are also presented. Thus, 2a and 2b catalyzed
     the dimerization of some terminal alkynes HC.tplbond.CR (R = Ph, CO2Et or
     SiMe3).
REFERENCE COUNT:
                          18
                                THERE ARE 18 CITED REFERENCES AVAILABLE FOR THIS
                                RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT
L15 ANSWER 8 OF 11 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER:
                          1997:402118 CAPLUS
DOCUMENT NUMBER:
                          127:144256
TITLE:
                         Hydride, dihydrogen, dinitrogen and related
                          complexes of ruthenium containing
                          the ligand hydrotris(pyrazolyl)borate. X-ray crystal
                          structure of [{HB(pz)3}Ru(η2-
```

bis(diisopropylphosphino)ethane)
AUTHOR(S):

Jimenez Tenorio, Manuel; Jimenez Tenorio, Miguel
Angel; Puerta, M. Carmen; Valerga, Pedro

H2) (dippe) ] [BPh4] (dippe = 1,2-

CORPORATE SOURCE: Dept. de Ciencia de Materiales e Ingenieria
Metalurgica y Quimica Inorganica, Facultad de

Ciencias, Universidad de Cadiz, Aptdo. 40, 11510,

Puerto Real, Cadiz, Spain

SOURCE: Inorganica Chimica Acta (1997), 259(1-2), 77-84

CODEN: ICHAA3; ISSN: 0020-1693

PUBLISHER: Elsevier
DOCUMENT TYPE: Journal
LANGUAGE: English

AB [{HB(pz)3}RuCl(PPh3)2] reacts with one equivalent of dippe (1,2-bis(diisopropylphosphino)ethane) in toluene to yield

[{HB(pz)3}RuCl(dippe)]. This compound reacts with NaBH4 in MeOH furnishing the monohydride [{HB(pz)3}RuH(dippe)], whereas [{HB(pz)3}RuH(PPh3)2] was obtained by reaction of [RuHCl(PPh3)3] with K[HB(pz)3]. Both monohydride complexes are protonated by HBF4 OEt2 at -80° to give the corresponding dihydrogen adducts [{HB(pz)3}Ru(H2)(dippe)]+ and [{HB(pz)3}Ru(H2)(PPh3)2]+, as inferred from longitudinal relaxation time (T1) and 1J(H,D) measurements. The latter complex is unstable and decomps. at room temperature, but the former is a stable species which does not rearrange to the dihydride form when the temperature is raised. The x-ray crystal structure of [{HB(pz)3}Ru(H2)(dippe)][BPh4] was determined (monoclinic, space group P21/c, R = 0.057). The dihydrogen ligand in this compound is

labile, and readily replaced by a range of neutral donor mols., yielding the corresponding complexes [ $\{HB(pz)3\}Ru(L)(dippe)\}$  [BPh4] (L = CO, CNBut, Me2CO, THF, N2). There is also supporting evidence for the formation of a

paramagnetic RuIII methoxide complex, [{HB(pz)3}Ru(OMe)(dippe)][BPh4]. All compds. were characterized by IR, NMR and microanal.

REFERENCE COUNT: 39 THERE ARE 39 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 9 OF 11 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1997:60763 CAPLUS

DOCUMENT NUMBER: 126:69230

AUTHOR (S):

SOURCE:

TITLE: Syntheses and Characterization of Hydrotris(1-

pyrazolyl)borate Dihydrogen Complexes of Ruthenium and

Their Roles in Catalytic Hydrogenation Reactions Chan, Wai-Chung; Lau, Chak-Po; Chen, Yu-Zhong; Fang,

Yi-Qun; Ng, Siu-Man; Jia, Guochen

CORPORATE SOURCE: Department of Applied Biology Chemical Technology,

Hong Kong Polytechnic University, Kowloon, Hong Kong

Organometallics (1997), 16(1), 34-44

CODEN: ORGND7; ISSN: 0276-7333

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

New hydrotris(1-pyrazolyl)borate complexes of ruthenium were synthesized. Reaction of RuCl(HB(pz)3)(PPh3)2 (1) with NaBH4 in ethanol produced the yellow monohydride complex RuH(HB (pz)3) (PPh3)2 (2). Protonation of 2 with HBF4·Et2O in dichloromethane gave the mol. dihydrogen complex [Ru(HB (pz)3)(PPh3)2(H2)]BF4 (3). Reactions of 3 with L produced [Ru(HB(pz)3)(PPh3)2(L)]BF4(L = CH3CN(4), H2O(5), N2). 3 Could be regenerated by reactions of 4 or 5 with pressurized H2. Deprotonation of 3 occurred with NEt3 or H2O under hydrogen pressure. Treatment of 1 with LiBF4 in acetonitrile produced the bis-solvento complex [Ru( HB(pz)3)(PPh3)(CH3CN)2]BF4 (6). Heating a THF/CH3CN (9/1) solution of 1 at 60° gave RuCl(HB(pz)3)(PPh3)(CH3CN) (7). Reaction of 7 with NaBH4 in THF produced the yellow monohydride complex RuH( HB(pz)3)(PPh3)(CH3CN) (8). Acidification of the monohydride 8 with HBF4 Et2O yielded [Ru(HB(pz)3)(PPh3)(CH3CN)(H2)]BF4 (9). Both complexes 4 and 6 are active catalysts for the hydrogenation of olefins in either anhydrous or hydrous THF. Enhanced catalytic activities were observed in the presence of water or NEt3. Deuterium was incorporated into the catalytic hydrogenation products when D2O was present in the reaction mixture The enhanced catalytic activity in the presence of water, and

explained with mechanisms which involve dihydrogen complexes.

REFERENCE COUNT: 73 THERE ARE 73 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

incorporation of deuterium in the hydrogenation products, could be best

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ACCESSION NUMBER: 93:45769 DISSABS Order Number: AAR9317299
TITLE: REACTIVITY OF (OXO) (PHOSPHINE) RUTHENIUM (IV) AND

(AQUA) (PHOSPHINE) RUTHENIUM (II) COMPLEXES:

MECHANISMS OF THE OXIDATION OF ORGANIC SUBSTRATES AND LIGAND SUBSTITUTION (ORGANIC SUBSTRATE OXIDATION, OXO(

PHOSPHINE) RUTHENIUM (IV), (AQUA) (PHOSPHINE

) RUTHENIUM (II) )

AUTHOR: ACQUAYE, JOHN HENRY [PH.D.]; TAKEUCHI, KENNETH J. [advisor]

CORPORATE SOURCE: STATE UNIVERSITY OF NEW YORK AT BUFFALO (0656)

SOURCE: Dissertation Abstracts International, (1993) Vol. 54, No.

4B, p. 1953. Order No.: AAR9317299. 169 pages.

DOCUMENT TYPE: Dissertation

FILE SEGMENT: DAI LANGUAGE: English

ENTRY DATE: Entered STN: 19930920

Last Updated on STN: 19930920

The reactivity of the oxo(phosphine)ruthenium(IV) complexes,  $\$  m\lbrack Ru(bpy)\sb2 (O)PR\sb3\rbrack (ClO\sb4)\sb2\\$ (where bpy = 2,2\\$\sp\prime\\$-bipyridine and \\$\rm PR\sb3 = P(C\sb6H\sb5)\sb3,\\$ P(p-\\$\rm C\sb6H\sb4CH\sb3)\sb3\\$, P(p-\\$\rm C\sb6H\sb4CH\sb3)\sb3\\$, P(p-\\$\rm C\sb6H\sb4CF\sb3)\sb3\\$, \\$\rm P(C\sb6H\sb4CF\sb3)\sb3\\$, in the oxidation of sulfides, sulfoxides, alcohols and teritary anilines was investigated. In addition, the aqua ligand substitution by acetonitrile in the (aqua) (phosphine) ruthenium(II) complexes was investigated in aqueous medium.

For the oxidation of sulfides to sulfoxides, an excellent correlation  $(R$\sp2$ = 0.99)$  was obtained between log  $(\k\sp\{\m X\}/k\sp\{\m H\}$)$  and the \$\sigma\$ values for the substituents of para-substituted thioanisoles (\$\rho\$ = \$-\$1.56). For the oxidation of sulfoxides to sulfones, a good correlation (R\$\sp2\$ = 0.98) was obtained between log (\$k\sb{\rm X/k\sb{\rm H}\$) and the \$\sigma\sp{+}\$ values for the substituents of para-substituted methyl phenyl sulfoxides (\$\rho\$ = \$-\$0.42). In addition, the kinetic isotope effect for the oxidation of thioanisole and methyl-\$d\sb3\$ phenyl sulfide produced \$k\sb{\rm H}/k\sb{\rm D}\$ = 1.14, and the oxidation of methyl phenyl sulfoxide and methyl-\$d\sb3\$ phenyl sulfoxide resulted in an inverse isotope effect of  $k\$  \m H}/k\sb{\rm D = 0.64. Hammett correlations of log ( $k\sb{\rm X}/k\sb{\rm Ym}$  H}\$) versus \$\Sigma\sigma\$ (where \$\sigma\$ is the Hammett substituent constant for each of the para-substituents on the triphenylphosphine ligands) also show linear relationships. The slopes of these plots gave  $\rho = 0.49$  $(R\$ \ p2\$ = 0.99)$  for the oxidation of thioanisole and  $\r$  = 0.37 (R $\sp2$  = 0.99) for the oxidation of methyl phenyl sulfoxide by the  ${\rm hem}{\c}$ results of all our experiments suggest that the rate determining step in the oxidation of thioanisole by \$\rm \lbrack Ru(bpy)\sb2(O)P(C\sb6H\sb5)\s b3\rbrack (Cl0\sb4)\sb2\$ involves primarily single electron transfer, whereas the rate determining step of the oxidation of methyl phenyl sulfoxide involves primarily an S\$\sb{\rm N}\$2 mechanism.

There were not good correlations for plots of  $\log k \$  \mathrm{X}/k\sb{\rm H}\$ versus the Hammett substituent constants \$\sigma, \sigma\sp+\$ or \$\sigma\sp{-}\$ for the oxidation of the para-substituted benzyl alcohols by \$\rm{\lbrack Ru(bpy)\sb2(0)P(C\sb6 H\sb5)\sb3\rbrack (Cl0\sb4)\sb2\\$. However, the plot of  $\log \rm{\{\t k}\sb{X}/{\t k}\$  \sigma\sp{\cdot}\$ versus \$\sigma\sp-\$ (where \$\sigma\sp{\cdot}\$ is the free radical stabilization constant), gave an excellent correlation with \$\rho\$ = \$-\$0.57, (R\$\sp2\$ = 0.99) for the oxidation of the para-substituted benzyl alcohols by (\$\rm{Ru(bpy)\sb2}(0)P(C\sb6 H\sb5)\sb3 \rbrack (Cl0\sb4)\sb2\\$ in methylene chloride. From these and other results, we propose a reaction pathway for the oxidation of benzyl alcohol by (oxo)ruthenium(IV) complexes which involves a partial hydrogen atom abstraction from the benzylic carbon in the rate determining step.

The features observed in the demethylation of the tertiary anilines by the (Ru(bpy)\$\sb2\$(O)(PR\$\sb3)\rbrack\sp{2+}\$ complexes resemble those of the cytochrome P-450 type oxygenation. (Abstract shortened by UMI.)

L15 ANSWER 11 OF 11 DISSABS COPYRIGHT (C) 2005 ProQuest Information and

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ACCESSION NUMBER: 93:32621 DISSABS Order Number: AAR9309867

PROTON-COUPLED ELECTRON TRANSFER AND MULTIELECTRON TITLE:

OXIDATIONS IN COMPLEXES OF RUTHENIUM AND OSMIUM DOVLETOGLOU, ANGELOS [PH.D.]; MEYER, THOMAS J. [advisor]

AUTHOR: CORPORATE SOURCE: THE UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL (0153) SOURCE: Dissertation Abstracts International, (1992) Vol. 54, No.

2B, p. 809. Order No.: AAR9309867. 285 pages.

DOCUMENT TYPE: Dissertation

FILE SEGMENT: DAI

English

LANGUAGE: ENTRY DATE:

Entered STN: 19930722

Last Updated on STN: 19930722

My doctoral research concerns the mechanism of proton-coupled AB electron transfer over an extended pH range. The impetus for this study derives from the importance of such processes in biological systems. These processes between ruthenium and osmium complexes and hydroquinones have been studied by using spectrophotometric methods and cyclic voltammetry. Elucidation of the mechanistic details has been attempted by using isotopic labelling, kinetic analyses, and numerical simulation of complex kinetic schemes.

The coordination and redox chemistry of polypyridyl-acetylacetonato and -oxalato complexes of ruthenium and the role of ancillary ligands in defining the properties of Ru\$\sp{\rm IV}\$O complexes were explored. These studies represent the first attempt to probe possible 2e $\sp-\$  oxidation by a Ru $\sp{\rm NT} \$  IV}\$0/Ru $\sp{\rm II}\$ OH\$\sb2\$ couple. Using a test ligand in the coordination sphere the net result of the acac\$\sp-\$ ligand affecting the electron density at the metal center was examined. It was found that acac\$\sp-\$ can act as a \$\sigma\$ donor, \$\pi\$ donor, and \$\pi\$ acceptor.

The synthesis and X-ray crystal structure of trans-(Ru\$\sp{\rm VI (tpy) (0) \$\sb2\$ (H\$\sb2\$0)) (Cl0\$\sb4) \sb2\$ are described. The complexes trans-(Ru(tpy)(0) $\sb2$ \$(H\$\sb2\$0)) \$\sp{2+}\$ and trans-(Ru(tpy)(0)\$\sb2\$\$(CH\$\sb3\$\$CN)) \$\sp{2+}\$\$ have been characterized by using UV-vis, \$\sp1\$H NMR, FTIR, and resonance Raman spectroscopy, and electrochemical techniques. Comparisons with the redox potentials for related couples and a thermodynamic analysis based on related ruthenium and structurally equivalent complexes of osmium revealed a number of features that will be useful in the rational design of metal ion redox catalysts.

A complex mechanistic study of a novel cis-directed four-electron oxidation by trans-Ru\$\sp{\rm VI}\$O\$\sb2\$ complexes involving double O-atom transfer to a single substrate was undertaken. The kinetics of nitrogen atom transfer reactions of an Os\$\sp{\rm VI}\$nitrido complex with phosphines was studied. A reactivity model was developed for metal-oxo epoxidation catalysts and cytochrome P-450, based on the kinetics and mechanisms of olefin epoxidation by  $Ru$\sp{\rm IV}$O and trans-Ru$\sp{\rm VI}$O$\sb2$.$ 

The  $((bpy) \sb2 (0) Ru \sp{\rm V} (\mu -0) Ru \sp{\rm V} (0) (bpy))$  $\Lambda_{+}\$  complex represents the only well-defined molecular catalyst for water oxidation. This work describes the synthesis, characterization, and redox chemistry of ((tpy)(C\$\sb2\$O\$\sb4\$)Ru\$\sp{\rm III}(\mu\$-O)Ru\$\sp{\rm III\$(C\$\sb2\$O\$\sb4\$)(tpy)) and ((tpy)(CO\$\sb3\$)Ru\$\sp{\rm III) (\mu\$-0) Ru $\sp{\rm III}$ \$ (CO\$\sb3\$) (tpy)). In acidic solutions the oxalato ligand is lost providing a convenient synthetic route to the cis-((tpy)(H\$\sb2\$0)\$\sb2\$Ru\$\sp{\rm III}\$(\$\mu\$-0)Ru\$\sp{\rm III} $(H$\sb2$0) \sb2$(tpy)) $\sp{4+}$.$ 

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DATE: Thursday, September 29, 2005

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	L6	L3 and (myoglobin   hemoglobin   hemoglobin   hemoglobin   catalase   cytochrome   \$  ferritin	27
,	L5	L3 and (apomyoglobin  apohemoglobin apohemeoxygenase apocatalase  apocytochrome apoferritin)	1
	L4	hydrogenation with cataly\$ same (ghodium  ruthenium  palladium  Pd) same complex\$ same (apomyoglobin  apohemoglobin apohemeoxygenase apocatalase  apocytochrome apoferritin)	0
	L3	hydrogenation with cataly\$ same (ghodium  ruthenium  palladium  Pd) same complex\$	2606
	L2	hydrogenation with cataly\$ same (ghodium  ruthenium  palladium  Pd)	29767
	L1	hydrogenation same cataly\$ same (ghodium  Ru ruthenium Ru  palladium  Pd)	33704

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	DB=B	PGPB,USPT,USOC; THES=ASSIGNEE; PLUR=YES; OP=ADJ	
	L5	(myoglobin hemoglobin hemeoxygenase catalase cytochrome ferritin) same ((rhodium  Rh ruthenium Ru palladium Pd) same (cavity  pocket? coordinat\$))	17
	L4	L3 and complex\$	141
	L3	L2 and (cavity  pocket? coordinat\$)	142
	L2	L1 and apo\$	187
	L1	(myoglobin hemoglobin hemeoxygenase catalase cytochrome ferritin) same (rhodium Rh ruthenium Ru palladium Pd)	437

END OF SEARCH HISTORY